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C O M P L E T E   S P E C I F I C A T I O N

FOR A STANDARD PATENT

O R I G I N A L

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Invention Title: "NEW METHOD OF PREPARING PRECIPITATED SILICA,
NEW PRECIPITATED SILICAS AND THEIR USE IN
REINFORCING ELASTOMERS"

The following statement is a full description of this invention,
including the best method of performing it known to us:-

The invention concerns a new method of preparing precipitated silica, some precipitated silicas which can be prepared by that method, precipitated silicas in the form of granules, powder or substantially spherical balls, and their application as a reinforcing filler for elastomers.

It is known that precipitated silica has long been used as a white reinforcing filler in elastomers and particularly in tyres.

Like any reinforcing filler however, it must be easy (a) to handle and (b) to incorporate, in mixtures.

In this respect use in powder form is not always satisfactory in that, purely from the point of view of handling and utilisation, it may lead to considerable dust formation and slow incorporation of the filler (low apparent density); furthermore, rubber mixing requires very accurate dosing operations, for which powder fillers are often unsuitable (pourability).

Use in granule form is certainly a suitable way of obviating the above disadvantages, but unfortunately it may often cause insufficient dispersion of the filler in the elastomer, and the degree of reinforcement finally achieved may be lower than could be obtained from a filler initially in powder form.

Generally speaking it is known that, if a filler is to provide optimum reinforcing properties, it must be present in the elastomer matrix in a final form which is both as finely divided as possible and as homogeneously distributed as possible. Now in the special case of the filler being introduced initially in granular form, such conditions can be brought about only insofar as (a) the granules have a very good capacity for incorporation in the matrix when mixed with the elastomer (incorporability of the granules) and for disintegration or deagglomeration in the form of a very fine powder (disintegration of the granules), and (b) the powder resulting from the said disintegrating process can in turn be dispersed completely and homogeneously in the elastomer (dispersion

of the powder). It will readily be appreciated that such requirements are incompatible or even conflict with the very nature of a granulate, considering its inherently dense, compact and resistant character and the relatively high cohesive energy linking

5 the constituent grains of silica. Preparation of granules of precipitated silica without sacrificing either mechanical strength or capacity for dispersion is today still a problem of compromise which is difficult to overcome.

Another difficulty is the fact that, for reasons for mutual

10 affinity, the silica particles (whether or not they emanate from previous disintegration of granules) have an unfortunate tendency to agglomerate within the elastomer matrix. These silica/silica interactions have the harmful effect of limiting the reinforcing properties to a level well below that which could theoretically be

15 achieved if all the silica/elastomer interactions which could be brought about during the mixing operation were in fact obtained. (The theoretical number of silica/elastomer interactions is known to be directly proportional to the external surface area or CTAB surface area of the silica used).

20 Moreover such silica/silica interactions tend to increase the stiffness and thickness of the mixtures, thus making them more difficult to use.

The invention aims to avoid the above disadvantages.

More specifically, its particular purpose is to propose a new

25 method of preparing precipitated silica with improved capacity for dispersion (and deagglomeration) and reinforcing properties. When used as a reinforcing filler for elastomers it must in particular give the elastomers mechanical properties, such as resistance to breaking, tearing and abrasion, which are

30 much improved compared with prior art silicas.

The invention also concerns some of the precipitated silicas which can be obtained by this method.

medium and, if appropriate, the rest of the silicate simultaneously,

and that the maximum proportion of dry material in the suspension immediately before drying is not more than 24%.

18. Precipitated silica, characterised in that it is in the form of granules with a BET specific surface area from 140 to 200 m^2/g, a CTAB specific surface area from 140 to 200 m^2/g, an attrition rate of less than 20% and a pore distribution such that the pore volume comprising pores from 175 to 275 Å in diameter is at least 60% of the pore volume comprising pores of no more than 400 Å in diameter.

47. The silica of any one of claims 36 to 46, characterised in that the balls have a mean size of at least 100 micron.

We, RHONE-POULENC CHIMIE, a French Company, being the person identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

Applicant: RHONE-POULENC CHIMIE

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Nominated Person: As above

Address: As above

Invention Title: "NEW METHOD OF PREPARING PRECIPITATED SILICA, NEW PRECIPITATED SILICAS AND THEIR USE IN REINFORCING ELASTOMERS"

Names of actual inventors: Yvonick Chevallier and Michel Rabeyrin

BASIC CONVENTION APPLICATION DETAILS:
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DATED this 24th Day of June, 1992
RHONE-POULENC CHIMIE

To: The Commissioner of Patents
      WODEN   ACT   2606

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NOTICE OF ENTITLEMENT

We, RHONE-POULENC CHIMIE of 25, Quai Paul Doumer, 92408, Courbevoie, Cedex, France, being the applicant in respect of Application No. 18536/92, state the following:-

1.   The person nominated for the grant of the patent has entitlement from the actual inventors:

If a patent were granted to the actual inventors in respect of the invention the nominated person would be entitled to have the patent assigned to it.

2.   The person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

3.   The basic application listed on the patent request form is the first application made in a Convention country in respect of the invention.

For and on behalf of
RHONE-POULENC CHIMIE

....Marc. DELENNE...............   ..JULY. 29,. 1992..............
                (Signature)   (Date)

Name: ....
Title: .Patent.Engineer...........

File: 16553

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NEW METHOD OF PREPARING PRECIPITATED SILICA, NEW PRECIPITATED SILICAS AND THEIR USE IN REINFORCING ELASTOMERS

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(56) Prior Art Documents
      AU 632806 54583/90
      US 4590052

(57) Claim

1.   A method of preparing precipitated silica with improved capacity for dispersion and reinforcing properties, of the type comprising reacting a silicate with an acidifying agent, whereby a suspension of precipitated silica is obtained, then separating and drying the suspension, characterised in that precipitation is carried out as follows:

(i)   by forming an initial sediment comprising at least part of the total quantity of silicate involved in the reaction and an electrolyte, the concentration of silica in said initial sediment being less than 100 g/l and the concentration of electrolyte in said initial sediment being less than 17 g/l,

(ii) by adding the acidifying agent to said sediment until a pH value for the reaction medium of at least about 7 is obtained,

(iii) by adding acidifying agent to the reaction

It also relates to precipitated silicas in the
form of granules, powder or substantially spherical
balls with improved capacity for dispersion (and
deagglomeration) and reinforcing properties.

5   It finally concerns the use of the precipitated
silicas as a reinforcing filler for elastomers,
particularly for tyres.

Thus one of the subjects of the invention is a
method of preparing precipitated silica with improved
10   capacity for dispersion and reinforcing properties, of
the type comprising reacting a silicate with an
acidifying agent, whereby a suspension of precipitated
silica is obtained, then separating and drying the
suspension, characterised in that precipitation is
15   carried out as follows:

(i)   by forming an initial sediment comprising
at least part of the total quantity of silicate involved
in the reaction and an electrolyte, the concentration of
silica in said initial sediment being
20   less than 100 g/l and the concentration of electrolyte
in said initial sediment being less than 17 g/l,

(ii)   by adding the acidifying agent to said
sediment until a pH value for the reaction medium of at
least about 7 is obtained,
25   (iii) by adding acidifying agent to the reaction
medium and, if appropriate, the rest of the silicate
simultaneously,

and that the maximum proportion of dry material
in the suspension immediately before drying is not more
30   than 24%.

Thus it has been found that a low concentration
of silica and electrolyte in the initial sediment (or
vessel bottoms) and an appropriate proportion of dry
material in the suspension to be dried were important
35   conditions to give the products obtained their excellent
properties.

It will be noted, broadly speaking, that the method in question is a method of synthesising precipitated silicate, that is to say, that an acidifying agent reacts on a silicate.

5　The acidifying agent and silicate are selected in a manner well known per se. It may be remembered that a strong inorganic acid such as sulphuric, nitric or hydrochloric or an organic acid such as acetic, formic or carboxylic is generally used as an acidifying agent.

10　The silicate used may be any common form, such metasilicates, disilicates and advantageously an alkali metal silicate, particularly sodium or potassium silicate.

In cases where sodium silicate is used it generally has an SiO_2/Na_2O weight ratio from 2 to 4:1 and more particularly from 3.0 to 3.7:1.

15　More particularly as far as the preparation method of the invention is concerned, precipitation is carried out in a specific manner, in the following stages.

A sediment (i.e. a vessel bottoms) is first formed, comprising silicate and an electrolyte. The quantity of silicate present in the sediment may be either the full quantity involved in the 20　reaction or only part of that quantity.

As far as the electrolyte is concerned, the term is understood here in its normal sense, i.e. any ionic or molecular substance which decomposes or dissociates when in solution, to form ions or charged particles.

25　A salt from the group comprising alkali metal and alkaline earth metal salts is used in particular, preferably the salt of the initial silicate metal and the acidifying agent, for example sodium sulphate in the case of a reaction between a sodium silicate and sulphuric acid.

An essential feature of the preparation method according to the invention is that the concentration of electrolyte in the initial sediment is less than 17 g/l and preferably less than 14 g/l.

Another essential feature of the method is that the concentration
5   of silica in the initial sediment is less than 100 g SiO, per litre. The concentration is preferably less than 80 g/l and especially less than 70 g/l. Particularly when the acid used for neutralisation is in a high concentration. especially over 70%, it is appropriate to work with an initial silicate sediment in which
10   the concentration of SiO, is below 80 g/l.

The porosity features of the silicas obtained are partly dependent on the conditions governing the concentration of electrolyte and silica in the initial sediment.

The second stage comprises adding the acidifying agent to the
15   sediment of the composition described above.

The addition of this agent, which leads to a correlated lowering of the pH of the reaction medium, is continued until a value of at least about 7, generally from 7 to 8, is reached.

Once this value is reached and in the case of an initial sediment
20   comprising only part of the full quantity of silicate involved, it is advantageous to add acidifying agent and the remainder of the silicate simultaneously.

The precipitation reaction proper is over when all the remaining quantity of silicate has been added.

25   It is advantageous to mature the reaction medium when precipitation is over and especially after the forementioned simultaneous addition; maturing may take, for example, from 5 minutes to 1 hour.

In all cases finally (that is to say, whether the initial sediment contains the full quantity of silica involved or only part of it), an additional quantity of acidifying agent may be added to the reaction medium after precipitation, in a possible subsequent

5   stage. The agent is generally added until a pH value from 3 to 6.5 and preferably from 4 to 6.5 is obtained. Its addition enables the pH of the final silica to be adjusted to the value required for a given application.

The temperature of the reaction medium is generally from 70 to

10   98°C.

In one embodiment of the invention the reaction is carried out at a constant temperature from 80 to 95°C. In a different embodiment the temperature at the end of the reaction is higher than at the beginning. Thus the temperature at the beginning of the reaction

15   is preferably kept at 70 to 95°C; it is then raised in a few minutes, preferably to 80 to 98°C, and kept at that level to the end of the reaction.

A silica pulp is obtained after the operations just described, and is then separated (liquid-solid separation). Separation

20   generally comprises filtration, if necessary followed by washing. Filtration may be effected by any suitable method, for example by filter press or band filter or rotating filter under vacuum

The suspension of precipitated silica thus recovered (filter cake)

25   is then dried.

An essential feature of the preparation method according to the invention is that the proportion of dry material in the suspension immediately before it is dried must be no more than 24% and preferably no more than 23% by weight.

30   Drying may be effected by any means known _per se_.

The preferred method is spray drying.

Any appropriate type of spray may be used for the purpose, especially turbine, nozzle, liquid pressure or dual fluid sprays.

In one form of the method of the invention the proportion of dry material in the suspension to be dried is over 18% and preferably over 20% by weight. In that case drying is generally carried out by a spray with diffusers.

The precipitated silica which can be obtained in accordance with this embodiment of the invention is advantageously in the form of substantially spherical balls, preferably of an average size of at least 80 micron; this is one of the subjects of the invention.

This content of dry material may be obtained in the actual filtering operation, by using a suitable filter which will give a filter cake with the correct content. In another method dry material, for example silica in powder form, is added to the cake to give the necessary content, in a subsequent stage of the process carried out after filtration.

It should be noted that the resultant cake is not generally in a condition which would allow it to be sprayed, mainly because of its excessively high viscosity; this is a well known fact.

The cake is then subjected to a disintegrating operation in a manner known per se. This may comprise passing the cake into a colloidal or ball-type mill. As a means of lowering the viscosity of the suspension to be sprayed, aluminium may be added during the process, particularly in the form of sodium aluminate as described in French patent FR-A-2536380, the teaching of which is included here. It may be added particularly at the actual disintegrating stage.

The drying operation may be followed by a stage of grinding the product recovered, particularly the product obtained by drying the suspension containing over 18% by weight of dry material. The precipitated silica which may then be obtained is advantageously

in the form of a powder, preferably of a mean size from 5 to 70 micron.

Products ground to the desired particle size may be separated from any products not of that size, for example by means of vibrating screens of appropriate mesh sizes; products not of the desired size which are thus recovered may be returned to the grinding operation.

Similarly, in another embodiment of the method of the invention, the suspension to be dried contains less than 18% by weight of dry material. Drying is generally effected by means of a turbine-type spray. The precipitated silica which can then be obtained in this embodiment is advantageously in the form of a powder, preferably of a mean size from 5 to 70 microns.

Precipitated silicas in the form of powders which can be obtained in an embodiment of the method of the invention preferably have a DOP oil absorption value from 180 to 350 ml/100g, for example from 200 to 345 ml/100g; they then form one of the subjects of the invention.

In another embodiment of the method, finally, the dried product (especially from a suspension containing less than 18% by weight of dry material) or the ground product may be subjected to an agglomeration stage.

Agglomeration is here understood as any method of linking finely divided objects to put them in the form of larger, mechanically resistant objects.

These methods are in particular dry compacting, direct compression, granulation by the moist method (i.e. using a binder such as water, silica slurry or the like) and extrusion. The arrangements and apparatus used to carry out such methods are well known per se and include, for example, compacting presses, pelleting machines,

rotating drum compacting machines, rotating granulators, and extruders.

In accordance with the invention the dry compacting method is preferred. For this purpose it is advantageous to use a drum-type
5 compacting machine, i.e. one in which compacting is effected by passing powdered product between two rolls which are under pressure and rotating in reverse directions. The pressure used is generally from 15 to 50 bars, preferably from 20 to 35 bars. The mechanical properties and especially the wear resistance of the products
10 obtained are broadly dependent on it.

When this method is applied it is found advantageous to deaerate the powdered products before proceeding to the compacting stage, so as to remove the air included in them. (The operation is also described as pre-densification or degassing). This preliminary
15 operation gives better control of the feeding of the products at the drums of the press and ensures more regular compacting. The deaeration may be carried out in apparatus which is well known per se, e.g. by passing powders between porous elements (plates or drums) equipped with a vacuum suction system.

20 Precipitated silica which can be obtained in this embodiment of the invention is advantageously in the form of granules, generally from 1 to 10 mm in size and preferably with an attrition rate of less than 20%. (The method of measuring the attrition rate is described below).

25 Contrary to what happens in prior art when operating on conventional silica powders, it will be noted that agglomeration of silica powders obtained according to the invention, by methods such as the above, has an eminently reversible character, in the sense that the granules obtained can still be disintegrated again,
30 in the form of a distinctive fine powder.

At the end of the agglomeration stage the products may be calibrated to a desired size, for example by screening, then packed for their future use.

Precipitated silica powders obtained in accordance with the
5   invention thus bring the advantage, _inter alia,_ of producing granules such as those mentioned above in a simple, effective and economic manner, especially through conventional shaping operations such as granulation or compacting. These operations do not cause any degradation which could mask or even destroy the excellent
10   reinforcing properties inherent in these powders, as may happen when conventional powders are used in prior art.

Other objects of the invention are new precipitated silicas in the form of granules, powder or substantially spherical balls with a capacity for dispersion (and deagglomeration) and outstanding
15   reinforcing properties.

In the following description the BET specific surface area is determined by the BRUNAUER - EMMET - TELLER method, described in "The journal of the American Chemical Society", vol.60, page 309, February 1938 and corresponding to NFT standard 45007 (November
20   1987).

The CTAB specific surface area is the external surface area determined in accordance with NFT standard 45007 (November 1987) (5.12).

DOP oil absorption is determined in accordance with NFT standard
25   30-022 (March 1953) using dioctylphthalate.

The filling density in the compacted state (DRT) is measured in accordance with NFT standard 030100.

It should finally be specified that the pore volumes given are measured by mercury porosimetry. The pore diameters are calculated
30   by the WASHBURN equation with an angle of contact theta equal to

130° and a surface tension gamma equal to 484 dynes/cm (MICROMERITICS 9300 porosity meter).

Thus a new precipitated silica is now proposed according to the invention. It is characterised in that it is in the form of
5 granules with a BET specific surface area from about 140 to 200 m2/g, a CTAB specific surface area from about 140 to 200 m2/g, an attrition rate of less than 20% and a pore distribution such that the pore volume comprising pores from 175 to 275 A in diameter is at least 60% of the pore volume comprising pores of no more than
10 400 A in diameter.

As mentioned above, such granules have a quite outstanding capacity for deagglomeration and dispersion. They further enable a far better compromise to be obtained between use and mechanical properties in the vulcanised state, than can be obtained in
15 practice with prior art silica granules, even those with an equivalent theoretical reinforcing power (i.e. a similar or identical CTAB external specific surface area).

Some of the structural features of the granules according to the invention will now be described.

20 As already mentioned, the granules according to the invention have a BET specific surface area from about 140 to 200 m2/g and preferably about 150 to 190 m2/g.

They further have a CTAB specific surface area from about 140 to 200 m2/g and preferably from 140 to 180 m2/g.

25 In a preferred embodiment of the invention the granules have a BET specific surface area/CTAB specific surface area ratio from 1.0 to 1.2:1, that is to say, they have low microporosity.

The granules according to the invention have a DOP oil absorption value generally from 150 to 350 ml/100g and more particularly from
30 180 to 300 ml/100g.

Another important feature of the silica granules of the invention
is their density. Their filling density in the compacted state
(DRT) is generally at least 0.27 and may be up to 0.37.

5 As for the porosity features of the granules according to the
invention, they generally have a total pore volume of at least
1 cm3/g and more particularly from 1.5 to 2 cm3/g.

One of the essential features of the granules according to the
invention is more specifically the pore volume distribution, and
more particularly the distribution of the pore volume generated by
10 pores no larger than 400 A in diameter. This volume is
particularly important, as it corresponds to the useful (or
effective) pore volume of the fillers used for reinforcing
elastomers. Analysis of porograms shows the granules according to
the invention to have an exceptional feature, viz that at least 60%
15 and preferably at least 65% of the useful pore volume is made up
of pores of a diameter within the specific range from 175 to 275A.

This extremely narrow distribution of the pore diameters generating
most of the useful pore volume appears to be the reason for the
exceptional capacity for dispersion shown by the granules according
20 to the invention as compared with prior art granules.

The inherent mechanical strength of the granules according to the
invention is ascertained and quantified by means of an attrition
test. This basically comprises subjecting the granules to a
specific crushing pressure then measuring the quantity of fines
25 produced; the quantity of fines corresponds to the attrition rate.

Still more specifically, the attrition rate is measured by the
following procedure: a sample batch of granules is previously
sieved on a 400 micron screen (RETSCH screening machine, VIBRO
model; stainless steel PROLABO screen; vibration time 5 mn;
30 vibration level 20). The granules left on the screen (screen
residue) are divided into three batches of similar mass, M1, M2 and
M3 (the selected masses are generally from 40 to 60 g). Each batch

is then crushed in a manual hydraulic press (FOG press) in the following manner:

    (i)   the batch is placed in a cylindrical receptacle (diameter 85 mm; thickness 2mm), then a smooth-surfaced metal cover is put gently over it

    (ii)   the piston of the press is brought onto the cover

    (iii) the piston is lowered until a force of 200 kg is obtained

    (iv) as soon as the crushing force of 200 kg is reached the piston is raised.

Each crushed batch is sieved on a 400 micron screen as before, except that the vibration time is set to 2 mn. The mass of the fine materials which have passed through the screen, m1, m2 and m3 respectively, is then measured.

A respective attrition rate is thus defined for each of the three batches:

$$RATE \; 1 = 100 \; m1/M1 \; (\%)$$
$$RATE \; 2 = 100 \; m2/M2 \; (\%)$$
$$RATE \; 3 = 100 \; m3/M3 \; (\%)$$

The mean of these three rates (i.e. (RATE 1 + RATE 2 + RATE 3)/3) defines the attrition rate of the initial sample.

The silica granules of the invention have an attrition rate of less than 20%. The rate is preferably less than 15%.

The attrition rate of the granules according to the invention is directly bound up with the intensity of the mechanical pressures which have previously been applied to agglomerate the particles of the initial powders, by methods defined in greater detail above. Even with very low attrition rates, however, the granules of the invention have the quite outstanding property of maintaining an excellent capacity for disintegration and dispersion.

This capacity can be quantified by two specific tests, one based on the action of the granules during grinding and the other on their rheological action after grinding.

Qualitatively, the capacity for disintegration may be assessed by
5   the ease or difficulty with which the granules can be put into a more finely divided form when subjected to an external mechanical action such as grinding.

This approach amounts to ascertaining the internal cohesive energy level of the granulate indirectly.

10   Quantitatively, the granules will have less cohesive energy and hence a greater capacity for disintegration to the extent that they lead to powders of a finer particle size, given an equal quantity of external energy supplied in mechanical form when they are ground.

15   Still more specifically, the grinding test is carried out by the following procedure:

Granules are fed continuously into a cutter-type mill (RETSCH mill, model ZM1) at a constant feed rate of 1.5 kg/h. In this apparatus grinding is effected by rotation of a metal ring with 24 cutters,
20   the rotar speed being set to 20 000 rpm, and an immobile metal grid (mesh diameter 0.5 mm) is arranged concentrically with the rotor but in the reverse of the normal position indicated by the manufacturer. The ground product is recovered continuously at the outlet of mill by means of a cyclone, then analysed.

25   The particle sizes of the powders thus recovered are determined by means of a laser granulometer (SYMPATEC), then the median diameter (D50) of the powders is measured.

In the test, powders recovered after their first passage through the mill can be returned to it for a second grinding, following
30   strictly the same procedure as above, and the operation can of

course be repeated as often as desired. After each passage through the mill the median diameter of the powder recovered is measured. By proceeding in this way it is possible to follow the evolution of the D50 of the powders as a function of the number of passages through the mill.

As will be seen from the examples below, the granules according to the invention have at least two important features which distinguish them from prior art granules: the first is that, after a single grinding operation, they already give very fine powders, i.e. powders with a D50 generally below 7 micron; the second is that, after a plurality of successive identical grinding operations, they give powders which display a regular, significant decrease in the D50, possibly down to a value of about 4 micron; in other words, the granules can be ground until the powder obtained has a particle size such that its D50 is about 4 micron. Such values indicate the excellent capacity for disintegration of the granules according to the invention. They are evidence that the composite obtained after mixing with the elastomer will be reinforced by a very fine, non-aggregated filler.

As a comparison, prior art granules which have been ground once give powders with a higher D50, of over 7.5 micron and generally of the order of 9 to 10 micron. Even if many subsequent grinding operations are carried out, it is not possible to bring the D50 down to a value below 6 micron.

Another important novel feature of the granules according to the invention is the rheological action of powders produced by disintegrating them.

This action is ascertained by means of BROOKFIELD viscosity metering, which conveys and quantifies the capacity for dispersion (or dispersibility) of the disintegrated granules. BROOKFIELD viscosity metering is carried out on products which have been ground as in the grinding test defined above, and the results are determined by the following procedure:

- preparing a dioctylphthalate solution containing 8% by weight of a silica powder as obtained after grinding
- making the mixture completely homogeneous by vigorous agitation (STROEBER agitator: 1 000 rpm for 10 mn)
- bringing the mixture to 20°C (thermostatically controlled bath), the temperature at which metering is to be effected
- measuring the viscosity of the mixtures by means of a BROOKFIELD RVT viscometer equipped with a N^0 3 or 4 mobile
- carrying out a first shear at 50 rpm for 2 mn, then a shear at 5 rpm for 3 mn, before taking the measurement.

When the granules of the invention have been ground they have extremely high BROOKFIELD viscosities. Even after one grinding operation powders with a BROOKFIELD viscosity preferably of at least 10 Pa.s. and especially of at least 13 Pa.s. are obtained. Furthermore, after a plurality of successive identical grinding operations, the granules lead to powders which show a regular, extremely significant increase in BROOKFIELD viscosity, possibly up to at least 30 Pa.s. In other words, the granules may be ground until a powder with a BROOKFIELD viscosity of at least 30 Pa.s. is obtained. These values convey the excellent capacity for dispersion of powders obtained after disintegration of the granules of the invention; they are evidence that a completely homogeneous mixture of fine particles of reinforcing silica and elastomeric matrix has been obtained.

As a comparison, prior art granules which have been ground once lead to powders with a BROOKFIELD viscosity below 10 Pa.s.; moreover, if a plurality of successive grinding operations are carried out, less evolution of the BROOKFIELD viscosity of the powders is observed, generally not in excess of 20 Pa.s.

The granules of the invention may be in many different forms. For example they may be spherical, cylindrical, parallelepipedal, in the form of tablets, wafers, pellets, extrusions of circular or polylobe section or other similar shapes. Their dimensions may be very varied, ranging e.g. from one to several millimetres,

generally from 1 to 10 mm, along the axis of their largest dimension (length); the length/width ratio (the width being defined as the dimension immediately below the length) may itself vary widely, generally from 1 to 10 and more particularly from 1 to 5.

The invention also proposes a new precipitated silica which is characterised in that it is in the form of a powder with a BET specific surface area from about 140 to 200 m2/g, a CTAB specific surface area from about 140 to 200 m2/g, a DOP oil absorption value from 180 to 350 ml/100g, and a pore distribution such that the pore volume made up of pores from 175 to 275 A in diameter constitutes at least 50% of the pore volume made up of pores no larger than 400A in diameter.

As already mentioned, such silicas are favoured precursors for synthesising the granules according to the invention, and apart from this fact they already have really important properties themselves. This applies especially to the significant improvement in the compromise between use and final mechanical properties which they provide over prior art silica powders.

Some of the structural features of the powders according to the invention will now be described.

The powders have a BET specific surface area from about 140 to 200 m2/g. It is preferably from 150 to 190 m2/g.

As for their CTAB specific surface area, it is also from about 140 to 200 m2/g. It is preferably from 140 to 180 m2/g.

In a special preferred embodiment, the powders have a BET specific surface area/CTAB specific surface area ratio from 1.0 to 1.2:1, that is to say, they are slightly microporous.

Their DOP oil absorption value is from 180 to 350 ml/100g and more particularly from 200 to 345 ml/100g.

As far as their filling density in the compacted state (DRT) is concerned, this is generally at least 0.17 and, for example, from 0.2 to 0.3.

As for the porosity properties of the silica powders according to the invention, these normally have a total pore volume of at least 2.5 cm3/g, and generally from 3 to 5 cm3/g.

As with the granules described above, one of the essential features of the silica powders according to the invention is the distribution of their pore volume. Analysis of porograms of the powders according to the invention shows that the pore volume made up of pores from 175 to 275 A in diameter in itself represents at least 50% of the pore volume generated by pores no more than 400A in diameter (useful pore volume). The forementioned pore volume preferably constitutes at least 60% of the useful pore volume.

The powders of the invention generally have a mean particle size (D50) from 5 to 70 micron, preferably from 10 to 30 micron. This corresponds to the particle size best adapted to their subsequent shaping.

As with the granules, the powders can be characterised by a grinding test and a viscosity test as defined earlier in the specification.

Thus after a first grinding operation a powder is obtained, with a median diameter (D50) preferably less than 7 micron, for example of the order of 6 micron and a BROOKFIELD viscosity preferably of at least 20 Pa.s., generally at least 30 Pa.s. As a comparison, generally a D50 of over 7.5 micron and a BROOKFIELD viscosity of less than 20 Pa.s. are obtained with precipitated silica powders in prior art.

The capacity for deagglomeration of the powders according to the invention may be quantified in a specific deagglomeration test.

The test is carried out as follows:

The cohesion of agglomerates is assessed by particle size metering (by laser diffraction), effected on a silica suspension which has previously been deagglomerated by ultrasonics; this measures the capacity of the silica for deagglomeration (breaking objects from 0.1 to some tens of microns). Ultrasonic deagglomeration is effected with a VIBRACELL BIOBLOCK (600 W) ultrasonic generator (sonificateur), fitted with a probe 19 mm in diameter. Particle size metering is carried out by laser diffraction on a SYMPATEC granulometer.

2 g of silica is weighed in a pillbox (height 6 cm, diameter 4 cm) and made up to 50 g with softened water; a 4% aqueous suspension of silica is made in this way and homogenised for 2 minutes by magnetic agitation. Ultrasonic deagglomeration is then carried out as follows: with the probe submerged to a length of 4 cm, the output power is adjusted so as to obtain a needle deviation on the power dial indicating 20% (corresponding to 120 watt/cm2 of energy dissipated by the wire end ferrule of the probe). Deagglomeration is effected for 420 seconds. The particle size is then measured when a known volume of the homogenised suspension (expressed in ml) has been put in the granulometer tank.

The lower the value obtained for the median diameter $\phi 50$, the higher will be the capacity of the silica for deagglomeration. The ratio of (10 x volume of suspension introduced) to the optical density of the suspension detected by granulometry is also determined (the optical density is of the order of 20%). This ratio indicates the proportion of fines, i.e. the proportion of particles smaller than 0.1 micron which are not detected by the granulometer. The higher this ratio, described as the ultrasonic deagglomeration factor (FD), the greater will be the silica's capacity for deagglomeration.

Silica in powder form according to the invention has an ultrasonic deagglomeration factor of over 6 ml and especially over 6.5 ml.

It also preferably has a median diameter ($\phi 50$) smaller than 4.5 micron and particularly smaller than 4 micron, after ultrasonic deagglomeration.

The excellent properties inherent in the silica powders according to the invention are preserved even after shaping.

The invention also proposes a new precipitated silica which is characterised in that it is in the form of substantially spherical balls (or beads) with a BET specific surface area from about 140 to 200 m2/g, a CTAB specific surface area from about 140 to 200 m2/g, a mean size of at least 80 micron and a pore distribution such that the pore volume made up of pores from 175 to 275 A in diameter represents at least 50% of the pore volume made up of pores no larger than 400 A in diameter.

As indicated above, such a silica in the form of substantially spherical balls, which are advantageously solid, homogeneous, non-dust-forming and easily poured, have a very good capacity for deagglomeration and dispersion. It further has excellent reinforcing properties. A silica of this type is also a favoured precursor for synthesising the powders and granulates according to the invention.

Some of the structural properties of the balls (or beads) according to the invention will now be described.

The balls have a BET specific surface area from about 140 to 200 m2/g. It is preferably from 150 to 190 m2/g.

As for their CTAB specific surface area, it is also from about 140 to 200 m2/g. It is preferably from 140 to 180 m2/g.

In a special preferred embodiment, these balls have a BET specific surface area/CTAB specific surface area ratio from 1.0 to 1.2:1, that is to say, they are slightly microporous.

Their DOP oil absorption value is generally from 180 to 400 ml/100g and preferably from 200 to 350 ml/100g.

Their filling density in the compacted state (DRT) is generally at least 0.17 and may, for example, be from 0.2 to 0.32.

5   The silica balls of the invention have a mean size of at least 80 micron.

In some embodiments of the invention, the mean size is at least 100 micron and may, for example, be at least 150 micron; it is generally no more than 300 micron and is preferably from 100 to 250
10   micron. The mean size is determined in accordance with standard NF X 11507 (December 1970) by screening dry and determining the diameter corresponding to a cumulative residue of 50%.

As for the porosity features of the silica balls according to the invention, these normally have a total pore volume of at least 2.5
15   cm3/g, and generally from 3 to 5 cm3/g.

As with the granules and powders described above, one of the essential features of the silica balls according to the invention is the distribution of their pore volume. Analysis of porograms of the balls according to the invention shows that the pore volume
20   made up of pores from 175 to 275 A in diameter in itself represents at least 50% of the pore volume generated by pores no larger than 400 A in diameter (useful pore volume). The forementioned pore volume preferably constitutes at least 60% of the useful pore volume.

25   As with the granules and powders, the balls can be characterised by a grinding test and a viscosity test as defined earlier in the specification.

Thus after a first grinding operation a powder is obtained, with a median diameter (D50) preferably less than 8.5 micron and a BROOKFIELD viscosity of preferably at least 13 Pa.s and generally at least 15 Pa.s.

Furthermore, after a plurality of successive identical grinding operations, the balls lead to powders which show a regular, extremely significant increase in BROOKFIELD viscosity, possibly up to at least 30 Pa.s. In other words, the balls may be ground until a powder with a BROOKFIELD viscosity of at least 30 Pa.s. is obtained.

As with the powders, the balls can be characterised by a deagglomeration test as defined earlier in the specification.

Thus silica in the form of substantially spherical balls according to the invention preferably has an ultrasonic deagglomeration factor of over 5.5 ml and especially over 6.4 ml.

It also preferably has a median diameter (φ50) smaller than 5 micron and in particular smaller than 4.5 micron, after ultrasonic deagglomeration.

The silicas of the invention may, for example, be obtained through an appropriate embodiment of the previously described preparation method according to the invention.

The silicas of the invention or those which can be obtained by the method of the invention find a particularly important application in the reinforcement of natural or synthetic elastomers, particularly tyres.

They especially produce a significant improvement in resistance to breaking, tearing and abrasion in tyres; this is particularly useful in the manufacture of tyre treads.

The following examples illustrate the invention but do not restrict its scope.

EXAMPLE 1

The following are placed in a stainless steel reactor equipped with a propellor-type agitating system and a double-jacketed heater:

    - 660 litres of water

- 11.6 kg of Na,SO, (electrolyte)

- 323 litres of aqueous sodium silicates, with an SiO_2/Na_2O weight ratio of 3.45:1 and a density at 20°C of 1.230.

5   The concentration of SiO_2 in the sediment (or vessel bottoms) is then 77 g/l. The mixture is brought to a temperature of 82°C and agitation is maintained. 395 litres of dilute sulphuric acid of a density at 20°C of 1.050 is added until a pH value of 7.5 is obtained in the reaction medium (measured at its temperature.)

10   The reaction temperature is 82°C during the first 15 minutes of the reaction; it is then brought from 82 to 95°C in about 15 minutes, and kept at 95°C to the end of the reaction.

77 litres of aqueous sodium silicate of the type described above and 106 litres of sulphuric acid, also of the type described above,

15   are then added to the reaction medium together. The simultaneous addition of acid and silicate is carried out in such a way that the pH of the reaction medium during their addition is kept constantly at 7.5 ± 0.1. When all the silicate has been introduced, introduction of the dilute acid is continued for 5 minutes at a

20   flow rate of 310 l/h.

The introduction of additional acid brings the pH of the medium to a value of 5.0.

The total reaction time is fixed at 85 minutes.

A pulp of precipitated silica is thus obtained. It is filtered and

25   washed by means of a filter press, so that a silica cake is finally recovered, with a loss of weight on combustion (perte au feu) of 79% (hence the proportion of dry material is 21% by weight).

The cake is fluidified by mechanical and chemical action (adding a quantity of sodium aluminate corresponding to an Al/SiO_2 weight

30   ratio of 3 000 ppm). After this disintegrating operation a cake

which can be pumped is obtained, at a pH of 6.3. It is then sprayed using a nozzle -type spray.

The product thus dried is then ground (FORPLEX percussion mill, model FL1; rotary speed 4 900 rpm) to obtain a mean particle size (D50) of the order of 16 micron.

The characteristics of silica P1 obtained in powder form (according to the invention) are then as follows:

- BET specific surface area   = 170 m2/g
- CTAB specific surface area   = 160 m2/g
- DOP oil absorption   = 300 ml/100 g
- DPT (filling density)   = 0.22
- pore volume V1 represented by
  pores of d<400 A   = 0.95 cm3/g
- pore volume V2 represented by
  pores 175 A<d<275 A   = 0.54 cm3/g
- V2/V1 ratio   = 57%

Silica P1 is subjected to grinding and rheology tests as defined earlier in the specification (RETSCH mill; throughput 1.5 kg/h; grid 0.5 mm).

After one passage through the mill the median diameter (D50) of the ground powder obtained is 6.1 micron. The BROOKFIELD viscosity of the ground powder is 32 Pa.s.

Silica P1 is also subjected to the deagglomeration test as defined earlier in the specification.

After ultrasonic deagglomeration, powder P1 has a median diameter (ϕ50) of 3.2 micron and an ultrasonic deagglomeration factor (FD) of 8.5 ml.

EXAMPLE 2

Two very common commercial silicas are studied as a comparison;
they are sold in powder form by DEGUSSA as reinforcing fillers for
elastomers:

5
- SIPERNAT° 22 powder (PC1)
- ULTRASIL VN3° powder (PC2)

The characteristics of these powders are set out in Table 1 below.
The table also contains the characteristics of powder P1 according
to the invention, as a comparison.

10
TABLE 1

	PC1	FC2	P1
BET s.s.a. (m2/g)	180	170	170
CTAB s.s.a. (m2/g)	160	155	160
DOP oil absorption (ml/100g)	300	260	300
DRT	0.27	0.20	0.22
V1 (cm3/g)	0.84	0.93	0.95
V2 (cm3/g)	0.36	0.43	0.54
V2/V1 (%)	43	46	57
D50 after 1 passage (micron)	9.8	7.6	6.1
BROOKFIELD viscosity (Pa.s.)	14	17	32
ϕ50 (micron)	7.4	9.9	3.2
Deagglomeration factor FD (ml)	3.0	2.3	8.5

EXAMPLE 3

Granules are prepared from the silica powder P1 in Example 1 by
compaction with a roller press.

The powders have previously been deaerated by means of a VACUPRESS
160/220 roller-type predensifier. The deaerated powders are then
fed continuously and at a constant flow rate into an ALEXANDERWERCK

WP 150/120 compacting press (roller diameter 150 mm; roller length 120 mm; rotary speed of rollers 12 rpm). The outlet of the press is equipped with a calibrating system which is adjusted so as to obtain compacted products of the order of 2 to 4 mm. The products are then passed onto a RHEVUM vibrating screen (grid aperture 1.5 x 4 mm) to separate them from the fines.

Three batches of granules according to the invention are prepared by following the above mode of operation. Only the compacting pressure applied by the rollers of the compacting press is varied. One then has:- a batch of granules compacted at 20 bars: GR 20
- a batch of granules compacted at 25 bars: GR 25
- a batch of granules compacted at 30 bars: GR 30

The characteristics of these granules are summarised in Table II. The table also gives the results of the grinding and BROOKFIELD viscosity tests after one passage through the RETSCH mill.

RATEM is the value of the attrition rate of the granules, measured in the test defined earlier in the specification.

TABLE II

	GR20	GR25	GR30	GRC1	GRC2
BET s.s.a. (m2/g)	170	170	170	180	170
CTAB s.s.a.(m2/g)	155	155	155	162	151
DOP oil absorption (ml/100g)	250	230	210	220	210
DRT	0.28	0.29	0.30	0.35	0.36
V1 (cm3/g)	0.88	0.88	0.88	0.89	0.88
V2 (cm3/g)	0.60	0.57	0.60	0.47	0.41
V_2/V_1 (%)	68	65	68	53	53
RATEM (%)	17.6	14.6	12.8	11.2	13
D50 after 1 passage (micron)	6.6	6.9	6.9	8.9	9.6
BROOKFIELD viscosity (Pa.s.)	17	16	12	7	6

EXAMPLE 4

Two batches of commercial silica granules (preparation methods unknown) are studied as a comparison:

- ULTRASIL VN3 GRANULAR* granules, marketed by DEGUSSA (GRC1)
- KS 404 GRANULAR* granules, marketed by AKZO (GRC2)

The characteristics of these granules are included in Table II above.

EXAMPLE 5

This example compares the evolution of the mean diameters (D50) and corresponding BROOKFIELD viscosities of powders obtained after a plurality of successive grinding operations (in tests as defined in the description), for granules GR25 (invention) and granules GRC1 (comparative).

The results are set out in Table III below.

TABLE III

Number of grinding operations	D50(μm)		BROOKFIELD viscosity(Pa.s)	
	GR25	GRC1	GR25	GRC1
1	6.9	8.9	16	7
2	5.1	8.7	19	7
3	4.7	8.6	25	8
4	4.3	8.4	27	7
5	4.1	8.3	33	7

EXAMPLE 6

This example illustrates the use and action of the granules according to the invention and the prior art granules in a formulation for industrial rubber.

5   The following formulation is used (in parts by weight):

S.B.R. 1509 rubber (1)   100
Silica granules   50
PERMANAX OD (2)   2
PEG 4000 (3)   3
10   ZnO ACTIF (4)   3
Stearic acid   3
Silane Si 69 (5)   5
Sulphur (6)   2.25
MBTS (7)   0.75
15   DUTG (8)   1.50

(1) styrene butadiene copolymer
(2) octylated diphenylamine (antioxidant)
(3) polyethylene glycol (silica/rubber interface agent)
(4) rubber quality zinc oxide (activator)
20   (5) silica/rubber coupling agent (product marketed by DEGUSSA)
(6) vulcanising agent
(7) benzothiazyl disulphide (vulcanisation accelerator)
(8) diorthotolylguanidine (vulcanisation accelerator)

The formulations are prepared as follows:

25   The following are inserted in an internal mixer (BANBURY type), in the order given and at the times indicated in brackets:
- SBR 1509 (to)
- the PEG 4000, the active ZnO, the Si 69, the PERMANAX OD and 2/3 of the silica (to + 1 mn)
30   - the stearic acid and the remainder of the silica (to + 2mn 30s)
- the MBTS and DOTG accelerators in the form of a master mix in SBR 1509 (to + 4 mn)

The material is discharged from the mixer when the temperature of the chamber reaches 130°C (i.e. approximately at to + 5 mn). The mixture is put into an open mill (mélangeur à cylindres) which is kept at 40°C, for calendering. The sulphur is put into the mill in the form of a master mix in SBR 1509. After homogenisation and three fine passes the final mixture is calendered in the form of sheets 2.5 to 3 mm thick.

The results of the tests are as follows:

1. Rheological properties

The readings are taken on the formulations in the crude state. The results are given in Table IV, which indicates the apparatus used to take the measurements.

TABLE IV

	GR20	GR25	GR30	GRC1	GRC2
MOONEY viscosity (1)	56.5	55	53.5	61	64
Min. couple (2)	8	7	8	10	10
Max. couple (2)	100	103	102	106	100
Modulus of elasticity(3)	1.45	1.40	1.35	1.75	1.65
Modulus of viscosity (3)	1.25	1.20	1.25	1.45	1.40

(1) MOONEY viscosity

(2) MONSANTO 100 S rheometer

(3) MONSANTO MDR 2000E rheometer

Formulations obtained with the granules of the invention systematically give the lowest values, both for MOONEY viscosity and for minimum couple and moduli of elasticity and viscosity.

This shows that mixtures prepared from the granules of the invention are easier to use, particularly in extrusion and calendering operations which are often carried out in tyre production . (Less energy is expended in using the mixture,

injection during the mixing process is easier, there is less swelling in the die during extrusion, less shrinkage during calendering, etc).

2. Mechanical properties

5   The measurements are taken on vulcanised formulations.

Vulcanisation is obtained by bringing the formulations to 150°C for 15 minutes.

The following standards are used:
  (i)   traction tests (moduli, breaking resistance):
10   NFT 46 002 or ISO 37-1977
  (ii)   angular tearing tests (100 °C):
         NFT 46-007
  (iii) abrasion resistance test
         DIN 53-516

15   The results obtained are set out in Table V.

TABLE V

	GR20	GR25	GR30	GRC1	GRC2
100% modulus (MPa)	3.2	3.0	3.1	3.4	3.2
300% modulus (MPa)	11.0	10.4	11.0	9.6	9.2
Reinforcement index (1)	3.4	3.4	3.5	2.8	2.8
Breaking resistance (MPa)	20.4	20.4	21.3	18.6	16.7
Abrasion resistance (2)	91	97	93	113	109
Resistance to angular tearing at 100°C (DaN/cm)	43	42	36	31	31.5

(1) Corresponds to the ratio: 300% modulus/100% modulus
(2) The lower the value measured, the better is the abrasion resistance.

The whole reaction is carried out at 90°C. 275 litres of dilute sulphuric acid with a density at 20°C of 1.050 is added to the mixture until a pH value of 7.5 (measured at 90°C) is obtained in the reaction medium.

5   53 litres of aqueous sodium silicate of the type described above and 79 g of sulphuric acid, also of the type described above, are then added to the reaction medium together. The simultaneous introduction of acid and silica is carried out in such a way that the pH of the reaction medium is constantly equal to 7.5 ± 0.1.

10   When all the silicate has been added the introduction of dilute acid is continued so as to bring the pH of the reaction medium to a value of 5.0.
The whole reaction takes 125 min.

A precipitated silica pulp is thus obtained and is filtered and

15   washed by means of a rotating filter under vacuum, so that the silica cake which is finally recovered has an 88% weight loss in combustion (and hence a proportion of dry material equal to 12% by weight).

The cake is fluidified simply by mechanical action. The resultant

20   pulp is sprayed using a turbine-type spray.

The characteristics of the silica P2 obtained in powder form (according to the invention) are then as follows:

- BET specific surface area   = 155 m2/g
- CTAB specific surface area   = 149 m2/g

25   - DOP oil absorption   = 330 ml/100g
- DRT   = 0.18
- pore volume V1 represented by
pores of d < 400 A   = 1.0 cm3/g
- pore volume V2 represented by

30   pores 175 A < d < 275 A   = 0.67 cm3/g
- V2/V1 ratio   = 67%

These last results clearly demonstrate the superior reinforcing effect imparted by the granules of the invention as compared with prior art granules, even those with an equivalent theoretic reinforcing power.

5   The granules of the invention give the lowest 100% moduli, which is proof of improved silica dispersion. But they also give the highest 300% moduli, which is proof of a higher density of silica/rubber interactions. They consequently give the highest reinforcement indices.

10   With regard to abrasion resistance, it will be noted that loss by abrasion is 10 to 20% lower than that suffered by the comparative granules. This is a very important advantage for the tyre application.

     The higher reinforcing power of the granules according to the
15   invention is also confirmed by the higher values obtained for resistance to breaking and tearing.

EXAMPLE 7

The following are placed in a stainless steel reactor equipped with a propellor-type agitating system and a double-jacketed heater:

20   - 772 litres of water
                                - 11 kg of Na_2SO_4 (electrolyte)
                                - 211 litres of aqueous sodium
                                  silicate, with an SiO_2/Na_2O weight
                                  ratio of 3.45:1 and a density at
25   20°C of 1.230.

The concentration of SiO_2 in the sediment is then 50 g/l. The mixture is brought to a temperature of 90°C and agitation is maintained.

Silica P2 is subjected to the grinding and rheology tests as defined earlier in the description (RETSCH mill; throughput 1.5 kg/h; grid 0.5 mm).

5 After one passage through the mill the median diameter (D50) of the ground powder obtained is 3.7 micron. The BROOKFIELD viscosity of the ground powder is 34 Pa.s.

Silica P2 is also subjected to the deagglomeration test as defined earlier in the specification.

10 After ultrasonic deagglomeration, powder P2 has a median diameter (ϕ50) of 2.7 micron and an ultrasonic deagglomeration factor (FD) of 9.5 ml.

EXAMPLE 8

The following are placed in a stainless steel reactor equipped with a propellor-type agitating system and a double-jacketed heater:

15 - 669 litres of water
- 11 kg of Na_2SO_4 (electrolyte)
- 314 litres of aqueous sodium silicate with an SiO_2/Na_2O weight ratio of 3.45:1 and a density at 20°C of 1.230.

20 The concentration of SiO_2 in the sediment is then 75 g/l. The mixture is brought to a temperature of 80°C and agitation is maintained. 400 l of dilute sulphuric acid with a density at 20°C of 1.050 is added until a pH value of 7.5 is obtained in the reaction medium. The temperature is 80°C for the first 45 minutes of the reaction; it is then brought from 80 to 85°C in less than 25 10 minutes and kept at 85°C to the end of the reaction.

Once a pH value of 7 is reached, 76 litres of aqueous sodium silicate of the type described above and 120 l of sulphuric acid, also of the type described above, are added to the reaction medium together. The simultaneous introduction of acid and silicate is 30 carried out in such a way that the pH of the reaction medium during the period of introduction is constantly equal to 7.5 ± 0.1. When all the silicate has been added, the introduction of dilute acid is continued for about 10 minutes so as to bring the pH of the reaction medium to a value of 4.5. The total length of the reaction is 120 mn.

A precipitated silica pulp is thus obtained and is filtered and washed by means of a rotating filter under vacuum, so that the silica cake which is finally recovered has an 87% weight loss in combustion (and hence a proportion of dry material equal to 13% by weight).

The cake is fluidified by mechanical and chemical action (adding a quantity of sodium aluminate corresponding to an Al/SiO_2 weight ratio of 4 000 ppm). After this disintegrating operation the pH of the cake is 6.5. The cake is sprayed using a turbine-type spray.

The characteristics of the silica P3 obtained in powder form (according to the invention) are then as follows:

- CTAB specific surface area   = 180 m2/g
- BET specific surface area   = 190 m2/g
- DOP oil absorption   = 345 ml/100g
- DRT   = 0.17
- pore volume V1 represented by
pores of d < 400 A   = 0.98 cm3/g
- pore volume V2 represented by
pores 175 A < d < 275 A   = 0.64 cm3/g
- V2/V1 ratio   = 65%

Silica P3 is subjected to the grinding and rheology tests as defined earlier in the description (RETSCH mill; throughput 1.5 kg/h; grid 0.5 mm).

After a single passage through the mill the median diameter D50) of the ground powder obtained is 6.5 micron. The BROOKFIELD viscosity of the ground powder is 25 Pa.s.

Silica P3 is also subjected to the deagglomeration test as defined earlier in the description.

After ultrasonic deagglomeration, powder P3 has a median diameter (ϕ50) of 3.6 micron and an ultrasonic deagglomeration factor (FD) of 7.1 ml.

EXAMPLE 9

5   Precipitation is carried out as described in Example 1.

The precipitated silica pulp obtained is filtered by means of a rotating filter under vacuum, so that the silica cake recovered has an 86% weight loss in combustion (and hence a proportion of dry material equal to 14% by weight).

10   The cake is fluidified by mechanical and chemical action (adding a quantity of sodium aluminate corresponding to an Al/SiO₂ weight ratio of 3 000 ppm). After this disintegrating operation the pH of the cake is 6.4. The cake is sprayed using a turbine-type spray.

15   The characteristics of silica P4 obtained in powder form (according to the invention) are then as follows:

- CTAB specific surface area	= 162 m2/g
- BET specific surface area	= 165 m2/g
- DOP oil absorption	= 345 ml/100g
20 - DRT	= 0.18
- pore volume V1 represented by pores of d < 400 A	= 0.90 cm3/g
- pore volume V2 represented by pores 175 A < d < 275 A	= 0.60 cm3/g
25 - V2/V1 ratio	= 66%

Silica P4 is subjected to the grinding and rheology tests as defined earlier in the description (RETSCH mill; throughput 1.5 kg/h; grid 0.5 mm).

After a single passage through the mill the median diameter D50 of the ground powder obtained is 5,7 microns. The BROOKFIELD viscosity of the ground powder is 32 Pa.s.

Silica P4 is also subjected to the deagglomeration test as defined earlier in the description.

After ultrasonic deagglomeration, powder P4 has a median diameter (ϕ50) of 2.5 micron and an ultrasonic deagglomeration factor (FD) of 10.5 ml.

EXAMPLE 10

This example illustrates the use and action of a powder according to the invention and a prior art powder in a formulation for industrial rubber.

The following formulation is used (in parts by weight):

S.B.R. 1509 rubber (1)	40
S.B.R.1778 rubber (2)	60
Silica	35
Active ZnO (3)	3
Stearic acid	9.7
C.B.S. (4)	2.3
D.P.G. (5)	1
Sulphur (6)	1.5
Silane Si 69 (7)	3.5

(1) styrene butadiene copolymer, type 1509
(2) "   "   "   type 1778
(3) rubber quality zinc oxide
(4) N-cyclohexyl 2-benzothiazyl sulphenamide
(5) Diphenyl guanidine
(6) vulcanising agent
(7) silica/rubber coupling agent (product marketed by DEGUSSA)

The formulations are prepared as follows:

The following are inserted in an internal mixer (BANBURY type), in the order given and at the times indicated in brackets:
- SBR 1509 and SBR 1778 (to)
5
- the active ZnO, the Si 69 and 2/3 of the silica (to + 1 mn)
- the stearic acid and the remainder of the silica (to + 2mn 30s)
- the CBS and DPG accelerators (to + 4 mn)

The material is discharged from the mixer when the temperature of the chamber reaches 130°C (i.e. approximately at to + 5 mn). The
10
mixture is put into an open mill (mélangeur à cylindres) which is kept at 40°C, for calendering. The sulphur is put into the mill.

After homogenisation and three fine passes the final mixture is calendered in the form of sheets 2.5 to 3 mm thick.

The results of the tests are as follows:

15
1. Rheological properties

The readings are taken on the formulations in the crude state at 150°C.

The results are given in Table VI, which indicates the apparatus used to take the measurements.

20
TABLE VI

	P4	PC2
Min. couple (1)	9.3	12.4
Max. couple (1)	86.5	90.6

(1) MONSANTO 100 S rheometer

The formulation obtained with the powder of the invention gives the lowest values.

This shows that mixtures prepared from the silica powder of the invention are easier to use.

5   Mechanical properties

The measurements are taken on vulcanised formulations.

Vulcanisation is obtained by bringing the formulations to 150°C for 15 minutes.

The standards used are indicated in Example 6.

10 The results obtained are set out in Table VII.

TABLE VII

	P4	PC2
100% modulus (MPa)	2	2.4
300% modulus (MPa)	8.4	7.6
15 Reinforcement index (1)	4.2	3.2
Breaking resistance(MPa)	12.8	9.7
Abrasion resistance (2)	78	97

(1) corresponds to the ratio: 300% modulus/100% modulus
(2) The lower the value measured, the better is the abrasion
20 resistance.

The above results clearly demonstrate the superior reinforcing effect imparted by the powder of the invention.

The powder according to the invention gives a lower 100% modulus, which is proof of improved silica dispersion. But it also gives
25 a higher 300% modulus, which is proof of a higher density of

silica/rubber interaction. It consequently gives a higher reinforcement index.

With regard to abrasion resistance, it will be noted that loss by abrasion is 20% lower than with the prior art powder.

5 The higher reinforcing power of the silica in powder form according to the invention is also confirmed by the high values obtained for resistance to breaking and tearing.

EXAMPLE 11

The following are placed in a stainless steel reactor equipped with
10 a propellor-type agitating system and a double-jacketed heater:

- 346 litres of water
- 7.5 kg of Na_2SO_4 (electrolyte)
- 587 litres of aqueous sodium silicate with an SiO_2/Na_2O weight ratio of 3.50:1 and a density at 20°C of 1.133.

15 The concentration of SiO_2 in the sediment is then 85 g/l. The mixture is brought to a temperature of 79°C and agitation is maintained. 386 l of dilute sulphuric acid with a density at 20°C of 1.050 is added until a pH value of 8 is obtained (measured at the temperature of the medium). The temperature of the reaction
20 medium is 79°C for the first 25 minutes of the reaction; it is then brought from 79 to 86°C in 15 minutes and kept at 86°C to the end of the reaction.

Once a pH value of 8 is reached, 82 litres of aqueous sodium silicate with an SiO_2/Na_2O weight ratio of 3.50:1 and a density at
25 20°C of 1.133, and 132 l of acid of the type described above, are added to the reaction medium together. The simultaneous introduction of acid and silicate is carried out in such a way that the pH of the reaction medium during the period of introduction is constantly equal to 8 ± 0.1. When all the silicate has been added,

the introduction of dilute acid is continued for 9 minutes so as
to bring the pH of the reaction medium to a value of 5.2.   The
introduction of acid is then stopped and agitation of the reaction
pulp is maintained for a further 5 mn.

5   The total length of the reaction is 118 mn.

A precipitated silica pulp is thus obtained and is filtered and
washed by means of a filter press, so that the silica cake which
is finally recovered has an 78.5% weight loss on combustion (and
hence a proportion of dry material equal to 21.5% by weight).

10   The cake is fluidified by mechanical and chemical action (adding
a quantity of sodium aluminate corresponding to an Al/SiO, weight
ratio of 3 000 ppm).   After this disintegrating operation a
pumpable cake with a pH of 6.5 is obtained.   The cake is sprayed
using a   nozzle-type spray.

15   The characteristics of the silica P5 obtained in the form of
substantially spherical balls (according to the invention) are then
as follows:

- CTAB specific surface area	= 158 m2/g
- BET specific surface area	= 166 m2/g
20 - DOP oil absorption	= 270 ml/100g
- DRT	= 0.28
- pore volume V1 represented by	
pores of d < 400 A	= 0.92 cm3/g
- pore volume V2 represented by	
25 pores 175 A < d < 275 A	= 0.57 cm3/g
- V2/V1 ratio	= 62%
- mean size of balls = 270 micron	

Silica P5 is subjected to the grinding and rheology tests as
defined earlier in the description (RETSCH mill;   throughput 1.5
30   kg/h; grid 0.5 cm).

After a single passage through the mill the median diameter D50) of the ground powder obtained is 8.4 micron. The BROOKFIELD viscosity of the ground powder is 19 Pa.s.

Silica P5 is also subjected to the deagglomeration test as defined
5 earlier in the description.

After ultrasonic deagglomeration, powder P5 has a median diameter (φ50) of 3.6 micron and an ultrasonic deagglomeration factor (FD) of 6.8 ml.

EXAMPLE 12

10 Precipation is carried out as described in Example 1.

The precipitated silica pulp obtained is also filtered by means of a   filter   press,   so that the silica cake recovered has a 79% weight loss on combustion (and hence a proportion of dry material equal to 21% by weight).

15 The cake is fluidified by mechanical and chemical action (adding a quantity of sodium aluminate corresponding to an Al/SiO_2 weight ratio of 3 000 ppm). After this disintegrating operation a pumpable cake with a pH of 6.3 is obtained. The cake is sprayed using a nozzle-type spray.

20 The characteristics of the silica P6 obtained in the form of substantially spherical balls (according to the invention) are then as follows:

- CTAB specific surface area   = 160 m2/g
- BET specific surface area   = 170 m2/g
25 - DOP oil absorption   = 276 ml/100g
- DRT   = 0.28
- pore volume V1 represented by
pores of d < 400 Å   = 0.90 cm3/g

- pore volume V2 represented by
pores 175 A < d < 275 A   = 0.55 cm3/g
- V2/V1 ratio   = 61%
- mean size of balls   = 260 micron

5 Silica P6 is subjected to the grinding and rheology tests as defined earlier in the description (RETSCH mill; throughput 1.5 kg/h; grid 0.5 mm).

After a single passage through the mill the median diameter (D50) of the ground powder obtained is 8.4 micron. The BROOKFIELD

10 viscosity of the ground powder is 18 Pa.s.

Silica P6 is also subjected to the deagglomeration test as defined earlier in the description.

After ultrasonic deagglomeration, powder P6 has a median diameter (ϕ50) of 4.3 micron and an ultrasonic deagglomeration factor (FD)

15 of 6.5 ml.

EXAMPLE 13

A commercial silica sold in the form of substantially spherical balls by RHONE-POULENC CHIMIE as a reinforcing filler for elastomers, in this case the silica ZEOSIL 175 MP (referred to as

20 MP1 below) is studied as a comparison.

The characteristics of these powders are set out in Table VIII below. The table also contains the characteristics of silica P6 according to the invention, as a comparison.

TABLE VIII

	MP1	P6
BET s.s.a. (m2/g)	175	170
CTAB s.s.a. (m2/g)	162	160
DOP oil absorption (ml/100g)	280	276
DRT	0.27	0.28
V1 (cm3/g)	0.95	0.90
V2 (cm3/g)	0.45	0.55
V2/V1 (%)	47	61
Mean size of balls (micron)	265	260
D50 after 1 passage (micron)	10.5	8.2
BROOKFIELD viscosity (Pa.s.)	7	18
ϕ50 (micron)	9.1	4.3
Deagglomeration factor FD (ml)	2.1	6.5

EXAMPLE 14

This example compares the evolution of the BROOKFIELD viscosities of powders obtained after a plurality of successive grinding operations (in tests as defined earlier in the description), for silica P6 (invention) and silicas MP1 and PC1 (comparative).

The results are set out in Table IX below.

TABLE IX

Number of grinding operations	BROOKFIELD viscosity(Pa.s)		
	P6	MP1	PC1
1	18	7	14
2	32	13	18
3	35	17	20
4	34	16	21
5	40	17	22

EXAMPLE 15

This example illustrates the use of balls according to the invention and prior art balls in a formulation for industrial rubber.

5   The formulation used is the same as that used in Example 10. The method of preparing it also corresponds to that described in Example 10.

The results of the tests are as follows:

1.   Rheological properties

10 The readings are taken on the formulations in the crude state at 150°C.

The results are given in Table X, which indicates the apparatus used to take the measurements.

TABLE X

	P6	MP1
Min. couple (1)	9.9	12.9
Max. couple (1)	90.3	94.5

(1) MONSANTO 100S rheometer

The formulation obtained with the balls of the invention give the
20 lowest values.

This shows that mixtures prepared from the silica balls of the invention are easier to use.

2. Mechanical properties

The measurements are taken on vulcanised formulations.

Vulcanisation is obtained by bringing the formulations to 150°C for 15 minutes.

5   The standards used were mentioned in Example 6.

The results obtained are set out in Table XI.

TABLE XI

	F6	MP1
100% modulus (MPa)	2.1	2.5
300% modulus (MPa)	8.7	8.5
Reinforcement index (1)	4.1	3.4
Breaking resistance (MPa)	12.4	10.4
Abrasion resistance (2)	82	90

(1) Corresponds to the ratio: 300% modulus/100% modulus

15 (2) The lower the value measured, the better the abrasion resistance.

The results below clearly demonstrate the superior reinforcing effect imparted by the balls of the invention.

The balls of the invention give a lower 100% modulus, which is 20 proof of improved silica dispersion. But they also give a higher 300% modulus, which is proof of a higher density of silica/rubber interactions.   They consequently give a higher reinforcement index.

With regard to abrasion resistance, loss by abrasion is 10% lower 25 than that suffered by prior art balls.

The higher reinforcing power of the silica in the form of substantially spherical balls according to the invention is also confirmed by the high value obtained for resistance to breaking.

EXAMPLE 16

5   The following are placed in a stainless steel reactor equipped with a propellor-type agitating system and a double-jacketed heater:

- 787 litres of water
- 13.2 kg of Na_2SO_4 (electrolyte)
- 196 litres of aqueous sodium silicate with an SiO_2/Na_2O weight
10 ratio of 3.52:1 and a density at 20°C of 1.230.

The concentration of SiO_2 in the sediment is then 47 g/l. The mixture is brought to 85°C and agitation is maintained.

The whole reaction is carried out at 85°C. 212 l of dilute sulphuric acid with a density at 20°C of 1.050 is added until a pH
15 value of 8 is obtained (measured at 85°C). 54 litres of aqueous sodium silicate of the type described above, and 75 l of sulphuric acid, also of the type described above, are added to the reaction medium together. The simultaneous introduction of acid and silicate is carried out in such a way that the pH of the reaction
20 medium is constantly equal to 8 ± 0.1.

When all the silicate has been added, the introduction of dilute acid is continued for 8 minutes so as to bring the pH of the reaction medium to a value of 5.2. The introduction of acid is then stopped and agitation of the reaction pulp is maintained for
25 a further 5 mn.

The total length of the reaction is 115 mn.

A precipitated silica pulp is thus obtained and is filtered and washed by means of a filter press, so that the silica cake which is finally recovered has an 79.5% weight loss on combustion (and hence a proportion of dry material equal to 20.5% by weight).

5   The cake is fluidified by mechanical and chemical action (adding a quantity of sodium aluminate corresponding to an Al/SiO_2 weight ratio of 4 000 ppm). After this disintegrating operation a pumpable cake with a pH of 6.4 is obtained. The cake is sprayed using a nozzle-type spray.

10   The characteristics of the silica P7 obtained in the form of substantially spherical balls (according to the invention) are then as follows:

- CTAB specific surface area	= 154 m2/g
- BET specific surface area	= 167 m2/g
15 - DOP oil absorption	= 282 ml/100g
- DRT	= 0.27
- pore volume V1 represented by pores of d < 400 A	= 0.90 cm3/g
- pore volume V2 represented by 20 pores 175 A < d < 275 A	= 0.57 cm3/g
- V2/V1 ratio	= 63%
- mean size of balls	= 270 micron

Silica P7 is subjected to the grinding and rheology tests as defined earlier in the description (RETSCH mill; throughput 1.5 25   kg/h; grid 0.5 mm).

After a single passage through the mill the median diameter (D50) of the ground powder obtained is 7.8 micron. The BROOKFIELD viscosity of the ground powder is 24 Pa.s.

Silica P7 is also subjected to the deagglomeration test as defined 30   earlier in the description.

After ultrasonic deagglomeration, powder P7 has a median diameter (φ50) of 3.2 micron and an ultrasonic deagglomeration factor (FD) of 8.6 ml.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1.   A method of preparing precipitated silica with improved capacity for dispersion and reinforcing properties, of the type comprising reacting a silicate with an acidifying agent, whereby a suspension of precipitated silica is obtained, then separating and drying the suspension, characterised in that precipitation is carried out as follows:

(i)   by forming an initial sediment comprising at least part of the total quantity of silicate involved in the reaction and an electrolyte, the concentration of silica in said initial sediment being less than 100 g/l and the concentration of electrolyte in said initial sediment being less than 17 g/l,

(ii) by adding the acidifying agent to said sediment until a pH value for the reaction medium of at least about 7 is obtained,

(iii) by adding acidifying agent to the reaction medium and, if appropriate, the rest of the silicate simultaneously,

and that the maximum proportion of dry material in the suspension immediately before drying is not more than 24%.

2.   The method of claim 1, characterised in that the concentration of electrolyte in the initial sediment is less than 14 g/l.

3.   The method of claim 1 or 2, characterised in that after the simultaneous addition of acidifying agent and the rest of the silicate, additional quantity of acidifying agent is added to the reaction medium.

4.   The method of claim 3, characterised in that the additional quantity acidifying agent is added until a pH value from 3 to 6.5 is obtained for the reaction medium.

5.   The method of claim 1 or 2, characterised in that the full quantity of silicate involved in the reaction is introduced at stage (i), and that acidifying agent is

- 50 -
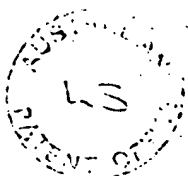
added at stage (iii) until a pH value from 3 to 6.5 is
obtained for the reaction medium.

6.   The method of any one of claims 1 to 5,
characterised in that the drying is effected by spraying.

5   7.   The method of claim 6, characterised in that a
suspension containing over 18% by weight of dry material
is dried.

8.   The method of claim 7, characterised in that a
suspension containing over 20% by weight of dry material

10   is dried.

9.   The method of claim 7 or 8, characterised in that
said drying is effected by means of a nozzle-type spray.

10.   The method of any one of claims 6 to 9,
ch acterised in that the dried product is then ground.

15   11.   The method of claim 6, characterised in that a
suspension containing less than 18% by weight of dry
material is dried.

12.   The method of claim 11, characterised in that
said drying is effected by means of a turbine-type spray.

20   13.   The method of claim 10, characterised in that the
ground product is then agglomerated.

14.   The method of claim 11 or 12, characterised in
that the dried product is then agglomerated.

15.   Precipitated silica in the form of substantially

25   spherical balls, which can be obtained by the method of
any one of claims 7 to 9.

16.   Precipitated silica in the form of a powder with
a DOP oil absorption value from 180 to 350 ml/100g,
which can be obtained by the method of any one of claims

30   10 to 12.

17.   Precipitated silica in the form of granules,
which can be obtained by the method of claim 13 or 14.

18.   Precipitated silica, characterised in that it is
in the form of granules with a BET specific surface area

35   from 140 to 200 m^2/g, a CTAB specific surface area from
140 to 200 m^2/g, an attrition rate of less than 20% and
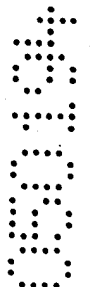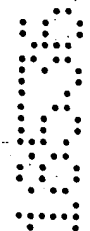
a pore distribution such that the pore volume comprising pores from 175 to 275 Å in diameter is at least 60% of the pore volume comprising pores of no more than 400 Å in diameter.

5   19.   The silica of claim 18, characterised in that said pore volume, made up of pores from 175 to 275 Å in diameter, represents at least 65% of said pore volume made up of pores no larger than 400 Å in diameter.

20.   The silica of claim 18 or 19, characterised in

10   that the granules have an attrition rate of less than 15%.

21.   The silica of any one of claims 18 to 20, characterised in that after a grinding operation the granules give a powder of a particle size such that its

15   median diameter (D50) is less than 7 micron.

22.   The silica of any one of claims 18 to 21, characterised in that said granules may be ground until a powder is obtained of a particle size such that its median diameter (D50) is 4 micron.

20   23.   The silica of any one of claims 18 to 22, characterised in that, after being ground, the granules give a powder with a BROOKFIELD viscosity of at least 10 Pa.s.

24.   The silica of claim 23, characterised in that the

25   viscosity is at least 13 Pa.s.

25.   The silica of any one of claims 18 to 24, characterised in that the granules may be ground until a powder with a BROOKFIELD viscosity of at least 30 Pa.s. is obtained.

30   26.   The silica of any one of claims 18 to 25, characterised in that the granules have a DOP oil absorption value from 150 to 350 ml/100g.

27.   The silica of claim 26, characterised in that the

35   DOP oil absorption value is from 180 to 300 ml 100g.

28.   The silica of any one of claims 18 to 27, characterised in that the granules are compacted

products, of a parallelepipedal shape and of a size from
1 to 10 mm.

29. Precipitated silica, characterised in that it is
in the form of a powder with a BET specific surface area
from 140 to 200 m^2/g, a CTAB specific surface area from
140 to 200m^2/g, a DOP oil absorption value from 180 to
350 ml/100g, and a pore distribution such that the pore
volume made up of pores from 175 to 275 Å in diameter
constitutes at least 50% of the pore volume made up of
pores no larger than 400 Å in diameter.

30. The silica of claim 29, characterised in that
said pore volume made up of pores from 175 to 275 Å in
diameter constitutes at least 60% of said pore volume
made up of pores no larger than 400 Å in diameter.

31. The silica of claim 29 or 30, characterised in
that, after being ground, it gives a powder of a
particle size such that its median diameter (D50) is
less than 7 micron.

32. The silica of any one of claims 29 to 31,
characterised in that, after being ground, it gives a
powder with a BROOKFIELD viscosity of at least 20 Pa.s.

33. The silica of claim 32, characterised in that the
viscosity is at least 30 Pa.s.

34. The silica of any one of claims 29 to 33,
characterised in that it has an ultrasonic
deagglomeration factor of over 6 ml.

35. The silica of any one of claims 29 to 34,
characterised in that, after ultrasonic deagglomeration,
it has a median diameter (ϕ50) of less than 4.5 micron.

36. Precipitated silica, characterised in that it is
in the form of substantially spherical balls with a BET
specific surface area from 140 to 200 m^2/g, a CTAB
specific surface area from 140 to 200 m^2/g, a mean size
of at least 80 micron and a pore distribution such that
the pore volume made up of pores from 175 to 275 Å in
diameter represents at least 50% of the pore volume made
up of pores no larger than 400 Å in diameter.

37.   The silica of claim 36, characterised in that the balls have a DOP oil absorption value from 180 to 400 ml/100g.

38.   The silica of claim 37, characterised in that the absorption value is from 200 to 350 ml/100g.

39.   The silica of any one of claims 36 to 38, characterised in that said pore volume made up of pores from 175 to 275 Å in diameter constitutes at least 60% of said pore volume made up of pores no larger than 400 Å in diameter.

40.   The silica of any one of claims 36 to 39, characterised in that, after being ground, the balls give a powder of a particle size such that its median diameter (D50) is less than 8.5 micron.

41.   The silica of any one of claims 36 to 40, characterised in that, after being ground, the balls give a powder with a BROOKFIELD viscosity of at least 13 Pa.s.

42.   The silica of claim 41, characterised in that the viscosity is at least 15 Pa.s.

43.   The silica of any one of claims 36 to 42, characterised in that the balls can be ground until a powder with a BROOKFIELD viscosity of at least 30 Pa.s. is obtained.

44.   The silica of any one of claims 36 to 43, characterised in that the balls have an ultrasonic deagglomeration factor of over 5.5 ml.

45.   The silica of claim 44, characterised in that the deagglomeration factor is over 6.4 ml.

46.   The silica of any one of claims 36 to 45, characterised in that, after ultrasonic deagglomeration, the balls have a median diameter (ϕ50) of less than 5 micron.

47.   The silica of any one of claims 36 to 46, characterised in that the balls have a mean size of at least 100 micron.

48.   The silica of claim 47, characterised in that the balls have a mean size of at least 150 micron.

49.   A method of reinforcing an elastomer, comprising mixing the elastomer with a reinforcing filler selected from a silica obtained by the method of any one of claims 1 to 14 or the silica of any one of claims 15 to

5   17.

50.   A method according to claim 49 wherein the elastomer is for a tyre.

51.   A method of reinforcing an elastomer, comprising mixing the elastomer with a reinforcing filler selected

10   from a silica in powder form according to any one of claims 29 to 35 or a silica in the form of substantially spherical balls according to any one of claims 36 to 48.

52.   A method according to claim 50 wherein the elastomer is for a tyre.

15   53.   A method according to claim 1 substantially as herein described with reference to any one of the examples but excluding any comparative examples therein.

54.   A precipitated silica according to claim 18, 28 or 36, substantially as herein described with reference

20   to any one of the examples but excluding any comparative examples therein.

DATED this 4th day of JANUARY, 1994

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ABSTRACT

The invention concerns a new method of preparing precipitated
silica, with improved capacity for dispersion and reinforcing
properties.

It also concerns novel silicas in the form of granules, powder or
5   substantially spherical balls. These silicas are characterised in
that they have a BET specific surface area and a CTAB specific
surface area both from 140 to 200 m2/g, and that the pore volume
made up of pores from 175 to 275 Å in diameter constitutes at least
50% of the pore volume made up of pores no larger than 400 Å in
10 diameter in the case of powders and balls, and at least 60% thereof
in the case of granules. In addition the granules have an
attrition rate of less than 20%, the powder has a DOP oil
absorption value from 180 to 350 ml/100g, and the balls have a mean
size of at least 80 micron.

15 The invention also concerns the use of said silicas as reinforcing
fillers for elastomers.

END